The Difference in Chemical Behavior of Free and Combined Water as Illustrated by the Saponification of Esters

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JAMES EUGENE LEVERING HOLMES

June, 1915

EASTON, PA.:
ESCHENBACH PRINTING CO.
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The Difference in Chemical Behavior of Free and Combined Water as Illustrated by the Saponification of Esters

INTRODUCTION

Jones and Anderson,[1] in their work on the absorption spectra of solutions, studied the absorption spectra of neodymium chloride in water, in methyl alcohol and in mixtures of these two solvents. They found two sets of absorption spectra corresponding, the one to the aqueous solution and the other to the alcoholic.

In the mixture of these solvents, both of these spectra were obtained when the water was present in smaller quantities than 15%. With decrease in the percentage of water, the alcoholic spectrum increased in intensity. The water spectrum and the alcohol spectrum were found to be quite different from one another, and do not change over into each other when the composition of the mixed solvent changes.

Similar results were obtained with neodymium nitrate and praseodymium chloride. These results showed that the solvent played an important part in the absorption of light by solutions. Jones and Anderson explained this fact on the basis of the solvate theory of solution proposed by Jones in 1900, that a part of the solvent combines with the dissolved substance, and that the solvated parts have different resonance from the unsolvated.

The work of Jones and Anderson was continued by Jones and Strong,[2] who studied a large number of salts in various solvents, to see if the solvent in general played a role in the absorption of light by solution. Most of their work was done

[1] *Carnegie Inst. Wash. Pub.* No. 110; *Amer. Chem. Journ.*, 41, 163 (1909).

[2] *Carnegie Inst. Wash. Pubs.* Nos. 130 and 160; *Amer. Chem. Journ.*, 43, 37, 224 (1910); 45, 1 (1910); 47, 27 (1912); *Phys. Zeit.*, 10, 449 (1909); *Phil. Mag.*, April, 1910; *Jour. chim. phys.*, 8, 131 (1910).

with salts of neodymium and uranium, since these substances had sharp absorption lines and bands. That the solvent has much to do with the absorbing power of the solution can be seen from the following table showing the wave length of the absorption lines of uranyl chloride in various solvents:

In water	λλ4025	4170	4315	4460	4560	4740	4920
In methyl alcohol	λλ4090	4220	4345	4465	4590	4760	4930
In ethyl alcohol	λλ4100	4250	..	4400	4580	4750	4900
In propyl alcohol	λλ4100	4230	..	4400	4580	4750	4910
In isopropyl alcohol	λλ4100	4250	..	4360	4560	4750	..
In butyl alcohol	λλ4100	4240	..	4390	4560	4750	4970
In isobutyl alcohol	λλ ..	..	..	4400	4560	4720	4900
In ether	λλ4040	4160	..	4300	4444	..	4630
In methyl ester	λλ4030	4160	4280	4440	4620	4990	4920
In glycerol	λλ4025	4140	4260	4400	4540	4720	5050
In formamid	λλ ..	..	..	4450	4650	..	4840

Solutions of uranyl chloride in such closely related solvents as propyl and isopropyl alcohols have, as is shown above, different absorption lines and bands.

Jones and Strong studied the absorption spectra of salts of neodymium, and found different absorption lines and bands for solutions of the salts in isomeric solvents. This is brought out in the following table:

Absorption Spectra of Neodymium Chloride

In water	λλ3390	3465	3505	3540	3560	..	..	..
In methyl and ethyl alcohols	λλ3475	3505	..	3560	..	..	..	..
In propyl alcohol	λλ3545	3460	3490	3510	3525	3540	3560	3580
In isopropyl alcohol	λλ3460	3510	3535	..	..	..	..	..
In butyl alcohol	λλ3450	3460	3492	3535	3545	3560	..	..
In isobutyl alcohol	λλ3455	3485	3515	3545	3570	..	..	..
In glycerol	λλ3520	3475	3550	..	..	..	..	..

The nitrate of neodymium was studied in the same way as the chloride. The absorption bands of neodymium nitrate were found to be practically the same as the absorption bands of neodymium chloride. This is strong evidence that the solvent plays an important part in the absorption of light by substances dissolved in it.

Jones and Strong studied the effect of rise in temperature

on the absorption spectra of solutions, and found that the absorption bands widened with rise in temperature. When the solution is cooled down, the original spectrum is obtained. This was explained by the initial solvates, broken down by the rise in temperature, being reformed on cooling.

Jones and Guy[1] studied the effect of dilution on absorption spectra, and found that the absorption bands widened as the concentration of the solution was increased. This is what we would expect, since a change in the concentration of the solution would mean a change in the complexity of the solvate. The more dilute the solution the more complex the individual aggregate; and this change in complexity should affect its power of resonance. Conversely, the more concentrated the solution, the simpler each individual solvate and the greater its power of resonance.

Jones and Guy studied the effect of the dissolved substance on the absorption of light by water. The absorptions of aqueous solutions of salts were compared with the absorption of a layer of water equal in depth to the water in the solution. Slightly hydrated salts, such as potassium chloride and ammonium chloride were found to have about the same absorption as water. On the other hand, strongly hydrated salts, as calcium and magnesium chloride, were found to be *far more transparent than pure water*. They explained this fact on the ground that combined water has less absorption than free water.

Jones, Shaeffer, and Paulus[2] repeated and elaborated the work of Jones and Guy, and found the above relations to be general.

The above physical difference in the action of combined and free water, in their power to absorb light, led us to study solutions of slightly hydrated salts and strongly hydrated salts to see if a corresponding chemical difference existed between water in the combined and in the free state—in other words, to study the effect of free water on some chemical

[1] *Carnegie Inst. Wash. Pub.* No. **190**; *Ann. der Phys.*, **43**, 555 (1914); *Amer. Chem. Journ.*, **41**, 1 (1913).

[2] *Phys. Zeit.*, **15**, 447 (1914).

reaction in which water is one of the reacting substances, a solution of a slightly hydrated salt containing an amount of water equal to the free water, and a solution of a hydrated salt containing an amount of water equal to the free water.

Reaction Chosen

Berthelot and Pean de Saint Gilles,[1] as early as 1862–65, showed that the formation of an ester from an alcohol and an acid

$$CH_3COOH + HOC_2H_5 \rightleftarrows CH_3COOC_2H_5 + H_2O$$

proceeded in a slow, progressive manner towards a limit; and that the speed of the reaction was dependent on the amounts of the substances present and on the temperature. This was also shown to be a reversible process.

The reaction of the saponification of an ester has been studied by Ostwald[2] and Reicher[3] as a method for determining the strengths of acids and bases.

Bases were found to saponify the ester more rapidly than acids. The strengths of the acids and bases determined by this method, agreed with the strengths as determined by conductivity.

In other words it is the hydroxyl ion of the base and the hydrogen ion of the acid which do the saponifying. The velocities of the reactions studied by Reicher and Ostwald were so much greater, on account of the large number of ions furnished by the acids and bases, in contrast with the small number of ions in those studied by Berthelot and Saint Gilles.

We decided to use the saponification of an ester in the study of the action of *free water* and *combined water* for the following reasons:

In the first place, as Berthelot and Saint Gilles showed, the speed of the reaction is dependent on the relative amounts of the substances used. By keeping the amount of the ester constant, we could study the effect of the water in solutions of salts containing the same amounts of water.

[1] *Ann. chim. phys.*, **14**, 437 (1878); **15**, 220 (1878); **65**, 385 (1862); **66**, 5, 110 (1862); **68**, 225 (1865).

[2] *Jour. prakt. Chem.*, **28**, 449 (1883); **35**, 112 (1887).

[3] *Lieb. Ann.*, **228**, 257 (1885).

Secondly, the reaction proceeds slowly and its velocity could, therefore, be easily measured.

Thirdly, the speed of the reaction is dependent on the temperature. However, as the temperature rises the hydrates become less complex. From the results obtained from the ester and pure water, as compared with those from solutions of the salts, we could study the effect of rise in temperature on the hydrated salts.

Historical

The effect of neutral salts on reaction velocities was studied first by Arrhenius,[1] who investigated the hydrolysis of ethyl acetate as effected by bases, and by bases in the presence of one of their salts. He found that in the case of 1/40 normal potassium hydroxide, sodium hydroxide, and barium hydroxide, the addition of their halogen salts decreased the velocity of the reaction, and that the addition of sulphates increased the velocity.

Sphor[2] studied the effect of neutral salts on the inversion of cane sugar by acids, and on the saponification of an ester by bases. He found that the addition of neutral salts increased the velocity of the former reaction, but diminished the velocity of the latter.

Arrhenius[3] also studied the influence of neutral salts on the inversion of cane sugar by acids, and obtained results similar to those found by Spohr. The effect of the salt was greater with dilute than with more concentrated acids.

Euler[4] obtained results very similar to those found by Spohr.

The above work led to the study of the effect of neutral salts when the acid and base were absent.

Smith[5] measured the dissociation of organic dibasic acids, by measuring the rate at which the acids invert cane sugar. He also studied the effect of neutral salts on the reaction when the acids were absent, and found that while salts of weak acids

[1] *Zeit. phys. Chem.*, **1**, 110 (1887).
[2] *Ibid.*, **2**, 194 (1888).
[3] *Ibid.*, **4**, 237 (1889).
[4] *Ibid.*, **32**, 348 (1900).
[5] *Ibid.*, **25**, 144 (1898).

did not affect the reaction differently from pure water, the salts of strong acids, such as potassium chloride, and sodium sulphate, produced a large effect.

Kellogg[1] studied the problem of the effect of neutral salts on the reaction velocity of the saponification of ethyl acetate. The ester and the solutions were sealed in glass tubes and placed in a constant temperature bath at 100°. The tubes were then opened and the contents titrated with phenolphthalein and sodium hydroxide. To get the amounts of the solutions of the salts which should contain an amount equal to the free water, the density of the salt solution was determined, its percentage of water content figured, and the amount to be added calculated. Kellogg found that in the more dilute solutions the specific influence of the salt is greater. As the solutions become more concentrated the increase in reaction velocity grows less, and in the case of four normal potassium chlorides the hydrolysis is slower than in pure water. He found a decrease in the accelerating power from potassium chloride, to potassium bromide, to potassium iodide, which is in the reverse order of their stability. The curves plotted with time and percentage hydrolysis as axes, are of the same general character, with a concentration of maximum accelerating power, which is 1.8 normal for potassium chloride, 0.5 normal for potassium bromide, and 0.25 normal for potassium iodide. Abnormally low results were found with potassium iodide, which he explained as due to the decomposition of the potassium iodate present by the acetic acid formed in the reaction

$$KIO_3 + 6KI + 6CH_3COOH \longrightarrow KI + 3I_2 + 6CH_3COOK + 3H_2O.$$

These solutions were found to be slightly colored, due to the iodine set free. By varying the time, Kellogg studied the reaction from the point where one percent of the ester was hydrolyzed, to practically complete hydrolysis.

The salt has two effects: the one in dilute solution being accelerating; the other, increasing as the concentration increases, retarding the reaction.

[1] *Jour. Amer. Chem. Soc.*, **31**, 403, 886 (1909).

Kellogg suggested several theories to explain this phenomenon.

One hypothesis is that the accelerating effect is due to the ionized salt, and the retardation is due to the undissociated salt. This would explain the decreasing acceleration with increasing concentration, as the ionized part increases slowly in proportion to the non-ionized part. It would also account for the facts found by the earlier investigators, that the salt of an acid had the greatest effect with dilute acids; since with a dilute acid we have a smaller number of common ions, and, therefore, a greater dissociation of the salt.

Kellogg also stated that the two effects might be functions of the ions: one of the potassium, the other of the halogen ion. This would account for the difference between the three salts which he used, but not for the difference between weak and strong solutions.

Euler's[1] suggestion would explain the dual effect. He assumes that the salt increases the reactive capacity of the water, the ions of the neutral salt combining with the solvent. The water around the ion of the salt is at a high tension, and we, therefore, would have a large number of $\overset{+}{H}$ and $\overset{-}{OH}$ ions. This would explain the larger effect of neutral salts with dilute acids. Spohr and Arrhenius held practically the same views as Euler.

Euler also suggested that intermediate compounds might be formed.

Arrhenius' older idea of the "active" and "inactive" forms of the ester, would explain all of the facts, the salt disturbing the equilibrium in favor of the "active" form.

In conclusion, Kellogg stated that no one theory could explain all of the facts, each having its merits and its disadvantages.

Henderson and Kellogg,[2] continuing the work of Kellogg, studied the chlorides of sodium, lithium, calcium, strontium, and barium, and the chloride and iodide of cadmium. They

[1] *Zeit. phys. Chem.*, **32**, 348 (1900).

[2] *Jour. Amer. Chem. Soc.*, **35**, 396 (1913).

measured the conductivity and viscosity of the solutions at the concentrations and temperature employed in the experiments, and from these calculated the degree of ionization.

The work was carried out under the same conditions employed by Kellogg. They found that all of the salts used, even at concentrations as low as 0.1 normal, increase the rate of the reaction. As the concentration of the salt increases, the effect becomes less, and, finally, when the solution becomes concentrated the salt has a retarding effect.

The curves they obtained for these salts were found to be very similar to those for the alkali chlorides, but showed a larger effect. Cadmium chloride and iodide were found to give a very large value, due probably to their hydrolysis, since they gave an acid reaction.

Henderson and Kellogg found that the salts which produced the greatest effect were those which were least ionized. From this they drew the conclusion, that the solution of the problem was to be sought in the effect of the non-ionized portion of the salt, rather than in the ionized portion. If the hydrolysis of the ester is controlled by the concentration of the salt molecules, the cause of the observed maximum[1] is easily explained; since as the total concentration of the salt increases, not only does the concentration of the molecules increase but the viscosity also varies. The maximum, then, was the resultant between the acceleration produced by the salt molecules which increase with the concentration, and the resistance to the contact of the ester and water, due to the increased viscosity.

Measurements of the H^+ and OH^- ions, had they been carried out, would have had an important bearing on Euler's[2] hypothesis; that at higher salt concentrations water is much more ionized than in dilute solutions, and it is the increase in the ions from water that accelerates the reaction.

Hydrolysis

The presence of hydrogen or hydroxyl ions other than those from water, must be guarded against with greatest care. Since

[1] *Jour. Amer. Chem. Soc.*, **31**, 886 (1909).

[2] *Zeit. phys. Chem.*, **32**, 348 (1900).

the ions from water are relatively so few in number, the introduction of ions from other sources would render the results of little value. Ions might easily be introduced in the ester and in the solutions of the salts. The ester must be distilled until it gives a neutral reaction. Salts of weak acids or weak bases cannot be used on account of hydrolysis.

$$\begin{array}{ccccc} KCN & \rightleftarrows & \overset{+}{K} & + & \overset{-}{CN} \\ HOH & \rightleftarrows & \overset{-}{OH} & + & \overset{+}{H} \\ & & \uparrow\downarrow & & \uparrow\downarrow \\ & & KOH & & HCN \end{array}$$

The hydrocyanic acid would dissociate very slightly, while the potassium hydroxide would be almost entirely dissociated, giving a large excess of $\overset{-}{OH}$ ions, and therefore, an alkaline reaction. The hydroxyl ions, being in large numbers as compared with the hydroxyl ions from the water, would vitiate the results. In the case of a salt of a weak base, we would find an acid reaction.

The hydrolysis of salts can be calculated from the formula of Arrhenius[1]

$$\frac{(\text{Salt})}{(\text{Acid}) \times (\text{Base})} = \frac{K \text{ acid}}{K\overline{OH}}$$

in which the salt, acid, and base represent the total concentrations, ionized, and non-ionized, at the point of equilibrium, and the K's are the ionization constants. Similar formulae were worked out by Walker,[2] for a salt of a weak base and a strong acid, and by Arrhenius for a salt of a weak acid and a weak base.

Where the ionization constant cannot be determined by conductivity measurements, other methods must be used.

Shields[3] employed the saponification of ethyl acetate and showed that with increasing dilution the hydrolysis increased.

Ley[4] used the saponification of methyl acetate, the inver-

[1] *Zeit. phys. Chem.*, **5**, 16 (1890).
[2] *Ibid.*, **4**, 319 (1889).
[3] *Ibid.*, **12**, 167 (1893).
[4] *Ibid.*, **30**, 193 (1899).

sion of cane sugar and the conductivity methods; and found that these three methods gave results which agreed very well with one another.

These, being the most general methods, are the only ones that need to be considered.

Since the reaction of the saponification of an ester has been used to measure the hydrolysis of salts such as potassium cyanide and aluminum chloride, which react basic and acidic with indicators, it is of primary importance that neutral salts be used.

Salts which give no reaction with litmus, according to Salm,[1] have a concentration of H^+ or OH^- ions less than 0.000001, which is so small that it is negligible.

We found that the salts of potassium sodium, lithium, magnesium, calcium, barium and strontium, with chlorine, bromine, iodine and the nitric and sulphuric acid radicles, gave no reaction with litmus. The acids have an ionization constant which is very nearly unity; and the weakest of the bases has so large a constant that if substituted in Walker's[2] formula the hydrolysis would be negligible.

Finally, Bruner[3] showed that the hydrolysis of solutions of the chlorides of potassium, lithium, barium, strontium, calcium, and magnesium was too small to be measured. He also showed that, in general, chlorides were most hydrolyzed, then nitrates, and least of all sulphates.

Therefore, in the solutions to be studied the effect due to hydrolysis can be neglected.

Statement of Problem

The plan was to investigate the difference in the velocities with which free water and combined water saponified an ester under the following conditions:

(1) Time and concentration of the salts kept constant, temperature varying.

[1] *Zeit. phys. Chem.*, **57**, 471 (1907).
[2] *Ibid.*, **4**, 319 (1889).
[3] *Ibid.*, **32**, 133 (1900).

(2) Concentration of the salts and temperature constant, time varying.

(3) Time and temperature constant, concentration of salts varying.

The conditions were so regulated that the percentage of ester saponified was always small—as the H^+ ions of the acid formed, being in relatively large numbers as compared with the H^+ ions from water, would suppress the ionization of water and themselves effect the saponification.

EXPERIMENTAL

Apparatus

The reactions were allowed to take place in one hundred cc. Jena bottles with ground-glass stoppers. These bottles were suspended in constant temperature baths, very similar to those employed by Davis and Putnam.[1] The thermometers were compared with a standardized thermometer. The temperatures of the baths were kept constant to within 0.02 of a degree. The baths were stirred at first by a gas engine, later by an electric motor.

The solutions were measured by means of carefully calibrated pipettes; 10 cc. burettes were used for measuring the ester, and fifty cc. burettes for titration purposes. All measuring flasks were made of Jena glass and were calibrated by weight. The solutions were always kept in Jena bottles.

Solutions

As stated before, only solutions which gave neutral reactions with litmus were used. The salts were Kahlbaum preparations, recrystallized. The solutions of slightly hydrated salts were made up by weight, the strongly hydrated salts by analysis and dilution to the required normality.

A concentration was chosen arbitrarily, such that solutions of all the salts to be investigated could be obtained, *i. e.*, two normal. Later it was found to be necessary to change this concentration to normal, using also the more dilute solutions,

[1] *Carnegie Inst. Wash. Pub.* No. **210**, 117 (1915).

half-normal and quarter-normal. The amount of the solution that contained an amount of water equal to the free water was determined as follows: 10 cc. of the solution were weighed, and from this the weight of 1 cc. was determined. The weight of the salt per cc. was subtracted from this weight, giving the weight of the water per cc. of the salt solution. By taking the reciprocal of this, the amount of the solution containing an amount of water equal to 1 cc. was obtained. The same trouble was found with solutions of potassium iodide and sodium iodide being colored, as Kellogg[1] describes. A drop of sodium thiosulphate was used to decolorize the solution before titrating, as the color obscured the change in the indicator. All solutions of the halogens were standardized as their silver salts. Calcium nitrate was converted into the oxide; magnesium nitrate into the pyrophosphate; strontium nitrate into the sulphate, and lithium nitrate into the sulphate by evaporating with sulphuric acid. Magnesium sulphate was standardized as barium sulphate, and the iodides of sodium and potassium were also determined gravimetrically.

The Esters

The ester first employed was ethyl acetate. After some preliminary work, this was discarded in favor of methyl acetate, since its solubility in some of the strong salt solutions was so slight as to give us a heterogeneous system. Methyl formate was also studied, to see if the results obtained with methyl acetate were of a general character, or specific to the ester in question. The esters, which were Kahlbaum preparations, were distilled several times until they boiled at the proper temperature, and their reaction was neutral. The methyl formate had to be distilled frequently, on account of its apparent instability.

The Base and the Indicator

The finding of the proper base and indicator to be used in titrating the acid formed, gave us quite a little trouble. Standard sulphuric acid was made up, and on analysis found to contain 0.01205 gram of sulphuric acid per cc. This was used

[1] *Jour. Amer. Chem. Soc.*, 31, 886 (1909).

to standardize the base, the comparison being repeated from time to time to see that the base did not undergo any change in concentration. The acid was also restandardized from time to time, no change in its concentration being noticed. The alkali used first was alcoholic sodium hydroxide, the indicator phenolphthalein. The precipitate of sodium carbonate was filtered from the alcoholic solution in an atmosphere free from carbon dioxide by a method similar to that employed by Morse.[1] The alkali was one-tenth normal. Great difficulty was experienced in obtaining good end points with the above base and indicator. This might be due to the saponification of the ester by the strong base, or to the unfitness of the indicator. We, therefore, decided to test out different indicators and bases.

We found the following results:

Ammonia and phenolphthalein:

10 cc. standard acid in presence of the ester—19.3 cc. of base used.

10 cc. standard acid—16.3 cc. of base.

Sodium hydroxide and phenolphthalein:

5 cc. H_2SO_4—strength unknown in presence of the ester—16.8 cc. of base used.

5 cc. H_2SO_4—strength unknown—13.60 cc. of base.

Ammonia and methyl orange:

5 cc. standard acid in presence of the ester—7.8 cc. of base used.

5 cc. standard acid—7.82 cc. of base.

Sodium hydroxide and methyl orange:

5 cc. standard acid in presence of the ester—12.60 cc. of base used.

5 cc. standard acid—12.55 cc. of base.

Sodium hydroxide and methyl orange:

5 cc. H_2SO_4—strength unknown in presence of the ester—14.5 cc. of base used.

5 cc. H_2SO_4—strength unknown—13.5 cc. of base.

[1] "Exercises in Quant. Chem.," p. 330.

Ammonia and methyl orange:

5 cc. H_2SO_4—strength unknown in presence of the ester—8.7 cc. of base used.

5 cc. H_2SO_4—strength unknown—8.6 cc. of base.

Ammonia and phenolphthalein:

5 cc. H_2SO_4—strength unknown in presence of the ester—9.4 cc. of base used.

5 cc. H_2SO_4—strength unknown—9.1 cc. of base.

Thus far, ammonia and methyl orange gave the best results. With sodium hydroxide the color of the indicator rapidly disappears on standing, due probably to saponification of the ester. Barium hydroxide has frequently been used for this purpose, therefore, we tried this base.

Barium hydroxide and phenolphthalein:

5 cc. H_2SO_4—strength unknown in presence of the ester—6.0 cc. of base used.

5 cc. H_2SO_4—strength unknown—5.8 cc. of base.

Barium hydroxide and methyl orange:

5 cc. H_2SO_4—strength unknown in presence of the ester—5.8 cc. of base used.

5 cc. H_2SO_4—strength unknown—5.7 cc. of base.

The color of the indicator did not persist with barium hydroxide. Therefore, we discarded this in favor of ammonium hydroxide. As regards acetic acid, methyl orange is the only common indicator that can be used.

Ammonia and methyl orange:

10 cc. acetic acid—strength unknown in presence of ester—0.2 cc. of base used.

10 cc. acetic acid—strength unknown—0.1 cc. of base.

Methyl orange is of little value since we should have obtained readings of about 8 or 10 cc. Morse suggests corallin, since this is a good indicator with organic acids.[1]

Ammonia and corallin:

10 cc. acetic acid—strength unknown in presence of ester—9.0 cc. base used; 9.0 cc. base used.

10 cc. acetic acid—strength unknown—9.1 cc. of base; 9.1 cc. of base.

[1] Morse, "Exercises in Quant. Chem.," p. 289; Glaser, "Indikatoren," p. 92.

To see if the addition of salts would affect the titration any, we titrated in the presence of the ester and a salt:

10 cc. acetic acid—strength unknown.

In presence of the ester and calcium chloride—9.05 cc. of base used.

In presence of the ester and potassium chloride—9.0 cc. of base used.

Ammonium hydroxide and alcoholic corallin are, then, the base and the indicator to be used.

At first, one-fifth normal ammonia was used, but this gave us such small volumes that we decided to use one-twentieth normal ammonia.

After preparing the solution of the base, it was found to be not quite one-twentieth normal, but to contain 0.00167732 gram per cc.

For use with the methyl formate a fifth-normal solution was made up which contained 0.007 gram per cc.

To see if the methods we were using were accurate, the following experiments were carried out:

0.0733 gram of glacial acetic acid was weighed out and titrated with ammonia, corallin being used as the indicator. The amount of acetic acid calculated from the titration was 0.0730 gram. We would then have an error of less than 0.5%. With other organic acids we found errors of less than 0.1%.

The results obtained with formic acid of about 98.5% purity were 0.4917 gram weighed out, and 0.4842 gram calculated from the titration, giving us an error of about 0.1%.

Method of Procedure

Solutions of the salts and the ester were measured into bottles, which were then placed in the baths. After the required time had elapsed, the bottles were removed from the baths, and their contents titrated against the standard base. We found, after a good deal of preliminary experimenting, that the most favorable conditions for work were: for the methyl acetate, 4 cc. of the ester to 30 cc. of water; 24 and 48 hours, 15, 25 and 35 degrees and normal, half-normal, and quarter-normal salt solutions. For the methyl formate, 2

cc. of the ester to 30 cc. of water, 4 and 8 hours, 15 and 25 degrees (b. p. of methyl formate, 32.3°) and the same concentrations of the salts as were used with the methyl acetate. The bottles, when taken out of the baths, were immediately chilled to retard the reaction. The time required for titrating was practically the same as that required for adding the ester; therefore, the results are comparable: 12 solutions were studied at a time, 6 being duplicates. Two bottles containing pure water and ester were included in the sets of 12 bottles, to act as standards, and to show that the conditions did not vary. The addition of the ester and the titration of the contents of the bottles were always carried on in the same order, *e. g.*, the bottle to which the ester was added first was titrated first. The methyl formate had to be measured at 15°, on account of its high vapor-tension. At first the titration was made in beakers; later it was found that the titration could be carried on very well in the bottle itself, thus eliminating a source of error. An electric motor was used for stirring the baths, since the hot air engine could not be run over night. When the baths were not stirred during the night, they varied as much as 0.3° or 0.4°, and the position of the bottles as regards the heating and cooling surfaces seemed to produce a marked effect. Normal solutions of sodium and potassium sulphates, and of barium nitrate, could not be prepared, since these salts were not sufficiently soluble; therefore, they were not studied. Cadmium and aluminum salts were discarded on account of their acid reaction, and ammonium salts because they suppressed to nearly half-value the ionization of the alkali used in the titration. The ammonium salt formed by the neutralization of the acid titrated with the base would also affect the ionization of the base if the reaction was allowed to proceed very far.

Calculations

The results are expressed in percentages of the ester decomposed. This was obtained as follows:

In the first place, the total amount of the ester per bottle was determined. From the mean weight of four 10 cc. portions, the weight per cc. of the methyl acetate was found to be 0.9257

gram, giving us 3.7028 grams as the total weight of the methyl acetate.

Then the weight of the ester, which, on saponification, would give enough acetic acid to neutralize 1 cc. of the standard one-twentieth normal ammonia, was calculated; 1 cc. of ammonia corresponded to a decomposition of 0.003543 gram of methyl acetate. Dividing this value by the total amount of the ester, 3.7028 grams, we find that 1 cc. of one-twentieth normal ammonia (0.001677 gram per cc.) represents *0.0957%* of the ester saponified.

To get the percentage saponification for each salt, it is only necessary to multiply the burette reading for each bottle by the factor 0.0957%.

For methyl formate we obtained the following values: The weight per cc. of ester, 0.9701 gram; the total weight of the ester, 1.9402 grams; the weight of the ester which, when saponified, corresponded to 1 cc. of the fifth-normal ammonia (per cc. 0.007 gram) is 0.001199 gram, and the percentage saponification, 0.618%.

Data

In the following tables of data, the methyl acetate per bottle is 4 cc. or 3.7028 grams; the methyl formate, 2 cc. or 1.9402 grams. Table II contains the results when the baths were not stirred over night, and these results have, therefore, a slight error. It was found that calcium chloride and potassium nitrate, on dilution, increase, then decrease the velocity of the reaction. Duplicate measurements were, therefore, made with new solutions, and the results recorded in Table IV. The data in Tables X and XI were obtained, using the same salt solutions. It was at this point that we decided to study methyl formate, also. For Tables XIII and XV, new solutions were used, since those earlier employed had not been preserved. The volumes of the solutions of the salts that contained 30 cc. of water, were calculated as described above, the water per cc. of the solution being the difference in weight between 1 cc. of the solution and the salt in 1 cc. The water used in preparing the solutions of the salts, bases and acid

had been carefully purified, and had a mean specific conductivity of 1.5×10^{-6} at 25°. This water was also used in recrystallizing the salts. In the tables of data the concentrations of the solutions of the salts are expressed as N, N/2 and N/4. Tables II, IV, VI, VIII and X give the percentages of the methyl acetate saponified; Tables XI, XIII and XV of the methyl formate. Duplicate measurements were made with fresh solutions of magnesium sulphate and strontium bromide, since the results obtained with these salts were very low as compared with the results from the other salts that contain a large amount of water of crystallization. The results found were, however, identical with those earlier obtained.

TABLE I

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of sol. cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N KCl	0.9717	1.029	30.87
N KNO_3	0.9610	1.041	31.23
N $CaCl_2$	0.9721	1.028	30.84
N $MgCl_2$	0.9806	1.020	30.60
N $SrCl_2$	0.9716	1.029	30.87
N/2 KCl	0.9846	1.016	30.48
N/2 KNO_3	0.9789	1.022	30.66
N/2 $CaCl_2$	0.9871	1.013	30.39
N/2 $MgCl_2$	0.9874	1.013	30.39
N/2 $SrCl_2$	0.9852	1.015	30.45
N/4 KCl	0.9910	1.009	30.27
N/4 KNO_3	0.9845	1.016	30.48
N/4 $CaCl_2$	0.9921	1.008	30.24
N/4 $MgCl_2$	0.9924	1.008	30.24
N/4 $SrCl_2$	0.9909	1.009	30.27

TABLE II

	Solutions N	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2	25° 24 hrs.	35° 24 hrs.	Solutions N/4	25° 24 hrs.
1.....	30 cc.	0.076	0.147	0.390	0.287	30 cc.	0.146	0.386	30 cc.	0.153
2.....	H_2O	0.076	0.145	0.392	0.289	H_2O	0.144	0.385	H_2O	0.152
3.....	30.87 cc.	0.100	0.224	0.720	0.516	30.48 cc.	0.206	0.669	30.27 cc.	0.196
4.....	KCl	0.100	0.222	0.722	0.513	KCl	0.206	0.666	KCl	0.198
5.....	31.23 cc.	0.099	0.194	0.611	0.431	30.66 cc.	0.201	0.612	30.48 cc.	0.177
6.....	KNO_3	0.097	0.196	0.614	0.431	KNO_3	0.201	0.613	KNO_3	0.177
7.....	30.84 cc.	0.119	0.387	1.68	1.03	30.39 cc.	0.400	1.35	30.24 cc.	0.278
8.....	$CaCl_2$	0.117	0.385	1.69	1.05	$CaCl_2$	0.398	1.36	$CaCl_2$	0.277
9.....	30.60 cc.	0.132	0.410	1.67	1.33	30.39 cc.	0.326	1.23	30.24 cc.	0.276
10.....	$MgCl_2$	0.134	0.411	1.67	1.30	$MgCl_2$	0.323	1.23	$MgCl_2$	0.276
11.....	30.87 cc.	0.130	0.378	1.41	0.992	30.45 cc.	0.297	1.12	30.27 cc.	0.236
12.....	$SrCl_2$	0.128	0.375	1.42	0.989	$SrCl_2$	0.297	1.12	$SrCl_2$	0.239

TABLE III

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of sol. cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N LiCl	0.9688	1.032	30.96
N KNO_3	0.9589	1.043	31.29
N NaCl	0.9811	1.019	30.57
N $CaCl_2$	0.9718	1.029	30.87
N $Ca(NO_3)_2$	0.9496	1.053	31.59
N/2 LiCl	0.9840	1.016	30.48
N/2 KNO_3	0.9802	1.020	30.60
N/2 NaCl	0.9903	1.010	30.30
N/2 $CaCl_2$	0.9868	1.013	30.39
N/2 $Ca(NO_3)_2$	0.9773	1.023	30.69
N/4 LiCl	0.9917	1.008	30.24
N/4 KNO_3	0.9870	1.013	30.39
N/4 NaCl	0.9931	1.007	30.21
N/4 $CaCl_2$	0.9909	1.009	30.27
N/4 $Ca(NO_3)_2$	0.9880	1.012	30.36

TABLE IV

	Solutions N	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2	25° 24 hrs.	35° 24 hrs.	Solutions N/4	25° 24 hrs.
1.....	30 cc.	0.083	0.154	0.394	0.296	30 cc.	0.153	0.391	30 cc.	0.152
2.....	H_2O	0.084	0.154	0.392	0.297	H_2O	0.153	0.390	H_2O	0.151
3.....	30.96 cc.	0.094	0.204	0.626	0.462	30.48 cc.	0.199	0.590	30.24 cc.	0.194
4.....	LiCl	0.093	0.203	0.624	0.464	LiCl	0.198	0.591	LiCl	0.194
5.....	31.29 cc.	0.099	0.215	0.631	0.457	30.60 cc.	0.213	0.632	30.39 cc.	0.212
6.....	KNO_3	0.100	0.214	0.633	0.456	KNO_3	0.212	0.634	KNO_3	0.211
7.....	30.57 cc.	0.109	0.247	0.808	0.590	30.30 cc.	0.241	0.746	30.21 cc.	0.222
8.....	NaCl	0.111	0.245	0.806	0.591	NaCl	0.242	0.745	NaCl	0.222
9.....	30.87 cc.	0.129	0.393	1.72	1.15	30.39 cc.	0.306	1.35	30.27 cc.	0.285
10.....	$CaCl_2$	0.131	0.395	1.71	1.16	$CaCl_2$	0.308	1.36	$CaCl_2$	0.284
11.....	31.59 cc.	0.129	0.330	1.32	0.860	30.69 cc.	0.310	1.12	30.36 cc.	0.270
12.....	$Ca(NO_3)_2$	0.126	0.333	1.34	0.861	$Ca(NO_3)_2$	0.308	1.12	$Ca(NO_3)_2$	0.269

TABLE V

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of solution cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N $NaNO_3$	0.9696	1.031	30.93
N NaBr	0.9728	1.028	30.84
N KBr	0.9642	1.037	31.11
N $BaCl_2$	0.9700	1.031	30.93
N $Mg(NO_3)_2$	0.9527	1.049	31.48
N/2 $NaNO_3$	0.9803	1.020	30.60
N/2 NaBr	0.9852	1.015	30.45
N/2 KBr	0.9804	1.020	30.60
N/2 $BaCl_2$	0.9842	1.016	30.48
N/2 $Mg(NO_3)_2$	0.9789	1.022	30.66
N/4 $NaNO_3$	0.9881	1.012	30.36
N/4 NaBr	0.9922	1.008	30.24
N/4 KBr	0.9868	1.013	30.39
N/4 $BaCl_2$	0.9917	1.008	30.24
N/4 $Mg(NO_3)_2$	0.9877	1.012	30.36

TABLE VI

	Solutions N	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2	25° 24 hrs.	35° 24 hrs.	Solutions N/4	25° 24 hrs.
1.....	30 cc.	0.086	0.155	0.394	0.296	30 cc.	0.153	0.394	30 cc.	0.153
2.....	H_2O	0.086	0.154	0.395	0.297	H_2O	0.155	0.393	H_2O	0.154
3.....	30.93 cc.	0.105	0.225	0.692	0.490	30.60 cc.	0.223	0.663	30.36 cc.	0.210
4.....	$NaNO_3$	0.105	0.224	0.691	0.488	$NaNO_3$	0.222	0.661	$NaNO_3$	0.211
5.....	30.84 cc.	0.104	0.228	0.703	0.517	30.45 cc.	0.222	0.660	30.24 cc.	0.210
6.....	NaBr	0.105	0.227	0.704	0.517	NaBr	0.223	0.661	NaBr	0.209
7.....	31.11 cc.	0.107	0.230	0.690	0.507	30.60 cc.	0.224	0.667	30.39 cc.	0.216
8.....	KBr	0.106	0.231	0.689	0.505	KBr	0.224	0.668	KBr	0.217
9.....	30.93 cc.	0.142	0.377	1.38	0.967	30.48 cc.	0.315	1.09	30.24 cc.	0.267
10.....	$BaCl_2$	0.144	0.377	1.37	0.965	$BaCl_2$	0.316	1.09	$BaCl_2$	0.268
11.....	31.48 cc.	0.126	0.326	1.35	0.883	30.66 cc.	0.285	1.13	30.36 cc.	0.261
12.....	$Mg(NO_3)_2$	0.125	0.325	1.36	0.885	$Mg(NO_3)_2$	0.286	1.14	$Mg(NO_3)_2$	0.263

TABLE VII

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of sol. cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N KI	0.9513	1.051	31.53
N NaI	0.9611	1.040	31.20
N $CaBr_2$	0.9597	1.042	31.26
N $MgSO_4$	0.9938	1.006	30.18
N $Sr(NO_3)_2$	0.9509	1.052	31.56
N/2 KI	0.9746	1.026	30.78
N/2 NaI	0.9809	1.019	30.57
N/2 $CaBr_2$	0.9825	1.018	30.54
N/2 $MgSO_4$	0.9950	1.005	30.15
N/2 $Sr(NO_3)_2$	0.9758	1.025	30.75
N/4 KI	0.9864	1.014	30.42
N/4 NaI	0.9904	1.010	30.30
N/4 $CaBr_2$	0.9891	1.011	30.33
N/4 $MgSO_4$	0.9958	1.004	30.12
N/4 $Sr(NO_3)_2$	0.9881	1.012	30.36

Table VIII

	Solutions N	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2	25° 24 hrs.	35° 24 hrs.	Solutions N/4	25° 24 hrs.
1.....	30 cc.	0.086	0.155	0.395	0.296	30 cc.	0.155	0.395	30 cc.	0.155
2.....	H_2O	0.086	0.155	0.394	0.296	H_2O	0.155	0.394	H_2O	0.154
3.....	31.53 cc.	0.030	0.038	0.057	0.048	30.78 cc.	0.073	0.172	30.42 cc.	0.136
4.....	KI	0.032	0.036	0.056	0.049	KI	0.073	0.172	KI	0.135
5.....	31.20 cc.	0.075	0.119	0.341	0.239	30.57 cc.	0.171	0.498	30.30 cc.	0.176
6.....	NaI	0.077	0.118	0.342	0.241	NaI	0.172	0.498	NaI	0.177
7.....	31.26 cc.	0.075	0.134	0.653	0.492	30.54 cc.	0.153	0.689	30.33 cc.	0.191
8.....	$CaBr_2$	0.073	0.132	0.651	0.494	$CaBr_2$	0.151	0.671	$CaBr_2$	0.192
9.....	30.18 cc.	0.095	0.166	0.406	0.346	30.15 cc.	0.150	0.372	30.12 cc.	0.138
10.....	$MgSO_4$	0.097	0.168	0.408	0.344	$MgSO_4$	0.148	0.374	$MgSO_4$	0.140
11.....	31.56 cc.	0.139	0.297	1.09	0.711	30.75 cc.	0.287	0.968	30.36 cc.	0.260
12.....	$Sr(NO_3)_2$	0.139	0.298	1.09	0.713	$Sr(NO_3)_2$	0.285	0.966	$Sr(NO_3)_2$	0.261

TABLE IX

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of sol. cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N LiBr	0.9739	1.027	30.81
N Li_2SO_4	0.9757	1.025	30.75
N $BaBr_2$	0.9529	1.049	31.47
N $SrBr_2$	0.9536	1.049	31.47
N $LiNO_3$	0.9673	1.034	31.02
N/2 LiBr	0.9849	1.015	30.45
N/2 Li_2SO_4	0.9882	1.012	30.36
N/2 $BaBr_2$	0.9761	1.025	30.75
N/2 $SrBr_2$	0.9765	1.024	30.72
N/2 $LiNO_3$	0.9825	1.018	30.54
N/4 LiBr	0.9928	1.007	30.21
N/4 Li_2SO_4	0.9940	1.006	30.18
N/4 $BaBr_2$	0.9871	1.013	30.39
N/4 $SrBr_2$	0.9870	1.013	30.39
N/4 $LiNO_3$	0.9891	1.011	30.33

Table X

	Solutions N	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2	25° 24 hrs.	35° 24 hrs.	Solutions N/4	25° 24 hrs.
1.....	30 cc.	0.087	0.153	0.392	0.297	30 cc.	0.153	0.392	30 cc.	0.153
2.....	H_2O	0.086	0.153	0.392	0.298	H_2O	0.154	0.392	H_2O	0.153
3.....	30.81 cc.	0.033	0.053	0.128	0.100	30.45 cc.	0.105	0.307	30.21 cc.	0.161
4.....	LiBr	0.033	0.053	0.129	0.099	LiBr	0.106	0.308	LiBr	0.160
5.....	30.75 cc.	0.103	0.153	0.306	0.278	30.36 cc.	0.149	0.297	30.18 cc.	0.139
6.....	Li_2SO_4	0.105	0.153	0.305	0.277	Li_2SO_4	0.151	0.299	Li_2SO_4	0.139
7.....	31.47 cc.	0.081	0.179	0.705	0.445	30.75 cc.	0.223	0.813	30.39 cc.	0.241
8.....	$BaBr_2$	0.081	0.177	0.707	0.446	$BaBr_2$	0.224	0.815	$BaBr_2$	0.239
9.....	31.47 cc.	0.075	0.096	0.250	0.190	30.72 cc.	0.130	0.387	30.39 cc.	0.164
10.....	$SrBr_2$	0.077	0.098	0.248	0.192	$SrBr_2$	0.128	0.385	$SrBr_2$	0.162
11.....	31.02 cc.	0.086	0.167	0.508	0.370	30.54 cc.	0.182	0.555	30.33 cc.	0.201
12.....	$LiNO_3$	0.086	0.168	0.510	0.371	$LiNO_3$	0.182	0.557	$LiNO_3$	0.200

Table XI

	Solutions N	15° 4 hrs.	25° 4 hrs.	15° 8 hrs.	Solutions N/2	15° 4 hrs.	Solutions N/4	15° 4 hrs.
1	30 cc. H_2O	0.668	3.89	2.58	30 cc. H_2O	0.680	30 cc. H_2O	0.667
2		0.667	3.90	2.60		0.686		0.661
3	30.81 cc. LiBr	0.309	5.26	2.56	30.45 cc. LiBr	0.650	30.21 cc. LiBr	0.927
4		0.296	5.24	2.56		0.643		0.939
5	30.75 cc. Li_2SO_4	0.742	3.96	3.80	30.36 cc. Li_2SO_4	0.667	30.18 cc. Li_2SO_4	0.618
6		0.742	3.97	3.78		0.661		0.605
7	31.47 cc. $BaBr_2$	0.754	9.27	4.76	30.75 cc. $BaBr_2$	1.05	30.39 cc. $BaBr_2$	1.42
8		0.747	9.27	4.76		1.07		1.43
9	31.47 cc. $SrBr_2$	0.278	3.47	1.78	30.72 cc. $SrBr_2$	0.590	30.39 cc. $SrBr_2$	0.990
10		0.279	3.45	1.80		0.588		0.988
11	31.02 cc. $LiNO_3$	0.865	6.74	4.44	30.54 cc. $LiNO_3$	1.02	30.33 cc. $LiNO_3$	1.11
12		0.865	6.72	4.45		1.02		1.12

TABLE XII

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of sol. cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N NaBr	0.9722	1.029	30.87
N KCl	0.9704	1.030	30.90
N $BaCl_2$	0.9703	1.031	30.93
N $Ca(NO_3)_2$	0.9494	1.053	31.59
N $MgSO_4$	0.9938	1.006	30.18
N/2 NaBr	0.9866	1.014	30.42
N/2 KCl	0.9850	1.015	30.45
N/2 $BaCl_2$	0.9842	1.016	30.48
N/2 $Ca(NO_3)_2$	0.9772	1.023	30.69
N/2 $MgSO_4$	0.9950	1.005	30.15
N/4 NaBr	0.9928	1.007	30.21
N/4 KCl	0.9912	1.009	30.27
N/4 $BaCl_2$	0.9922	1.008	30.24
N/4 $Ca(NO_3)_2$	0.9883	1.012	30.36
N/4 $MgSO_4$	0.9958	1.004	30.12

TABLE XIII

	Solutions N	15° 4 hrs.	25° 4 hrs.	15° 8 hrs.	Solutions N/2	15° 4 hrs.	Solutions N/4	15° 4 hrs.
1	30 cc.	0.661	3.87	2.58	30 cc.	0.680	30 cc.	0.680
2	H_2O	0.667	3.90	2.60	H_2O	0.680	H_2O	0.680
3	30.87 cc.	1.05	7.00	4.25	30.42 cc.	0.988	30.21 cc.	0.927
4	NaBr	1.06	6.98	4.26	NaBr	0.988	NaBr	0.929
5	30.90 cc.	1.11	7.05	4.33	30.45 cc.	1.11	30.27 cc.	1.05
6	KCl	1.12	7.06	4.32	KCl	1.10	KCl	1.04
7	30.93 cc.	1.78	13.71	7.23	30.48 cc.	1.71	30.24 cc.	1.47
8	$BaCl_2$	1.76	13.70	7.22	$BaCl_2$	1.69	$BaCl_2$	1.45
9	31.59 cc.	1.24	9.86	5.25	30.69 cc.	1.17	30.36 cc.	1.11
10	$Ca(NO_3)_2$	1.25	9.84	5.24	$Ca(NO_3)_2$	1.19	$Ca(NO_3)_2$	1.13
11	30.18 cc.	1.36	8.50	5.92	30.15 cc.	1.10	30.12 cc.	0.926
12	$MgSO_4$	1.37	8.49	5.94	$MgSO_4$	1.12	$MgSO_4$	0.928

TABLE XIV

Solutions of the salts	Gram of H_2O per cc. of the sol.	Vol. of sol. cont. 1 cc. H_2O	Vol. of sol. cont. 30 cc. H_2O
N KI	0.9508	1.052	31.56
N $CaBr_2$	0.9599	1.042	31.26
N $SrCl_2$	0.9719	1.029	30.87
N $CaCl_2$	0.9718	1.029	30.87
N $Mg(NO_3)_2$	0.9529	1.049	31.48
N/2 KI	0.9741	1.027	30.81
N/2 $CaBr_2$	0.9823	1.018	30.54
N/2 $SrCl_2$	0.9852	1.015	30.45
N/2 $CaCl_2$	0.9870	1.013	30.39
N/2 $Mg(NO_3)_2$	0.9787	1.022	30.66
N/4 KI	0.9854	1.014	30.42
N/4 $CaBr_2$	0.9894	1.011	30.33
N/4 $SrCl_2$	0.9914	1.009	30.27
N/4 $CaCl_2$	0.9912	1.009	30.27
N/4 $Mg(NO_3)_2$	0.9877	1.012	30.36

TABLE XV

	Solutions N	15° 4 hrs.	25° 4 hrs.	15° 8 hrs.	Solutions N/2	15° 4 hrs.	Solutions N/4	15° 4 hrs.
1	30 cc.	0.670	3.89	2.60	30 cc.	0.661	30 cc.	0.680
2	H_2O	0.667	3.91	2.58	H_2O	0.667	H_2O	0.680
3	31.56 cc.	0.192	2.14	1.09	30.81 cc.	0.494	30.42 cc.	0.667
4	KI	0.188	2.14	1.08	KI	0.501	KI	0.668
5	31.26 cc.	0.618	8.59	4.73	30.54 cc.	0.982	30.33 cc.	1.03
6	$CaBr_2$	0.618	8.61	4.71	$CaBr_2$	0.984	$CaBr_2$	1.05
7	30.87 cc.	2.55	17.44	10.69	30.45 cc.	1.98	30.27 cc.	1.64
8	$SrCl_2$	2.56	17.42	10.71	$SrCl_2$	1.98	$SrCl_2$	1.63
9	30.87 cc.	2.97	19.86	12.74	30.39 cc.	2.18	30.27 cc.	1.85
10	$CaCl_2$	2.97	19.84	12.76	$CaCl_2$	2.19	$CaCl_2$	1.84
11	31.48 cc.	2.52	17.92	11.31	30.66 cc.	2.02	30.36 cc.	1.75
12	$Mg(NO_3)_2$	2.54	17.94	11.33	$Mg(NO_3)_2$	2.01	$Mg(NO_3)_2$	1.74

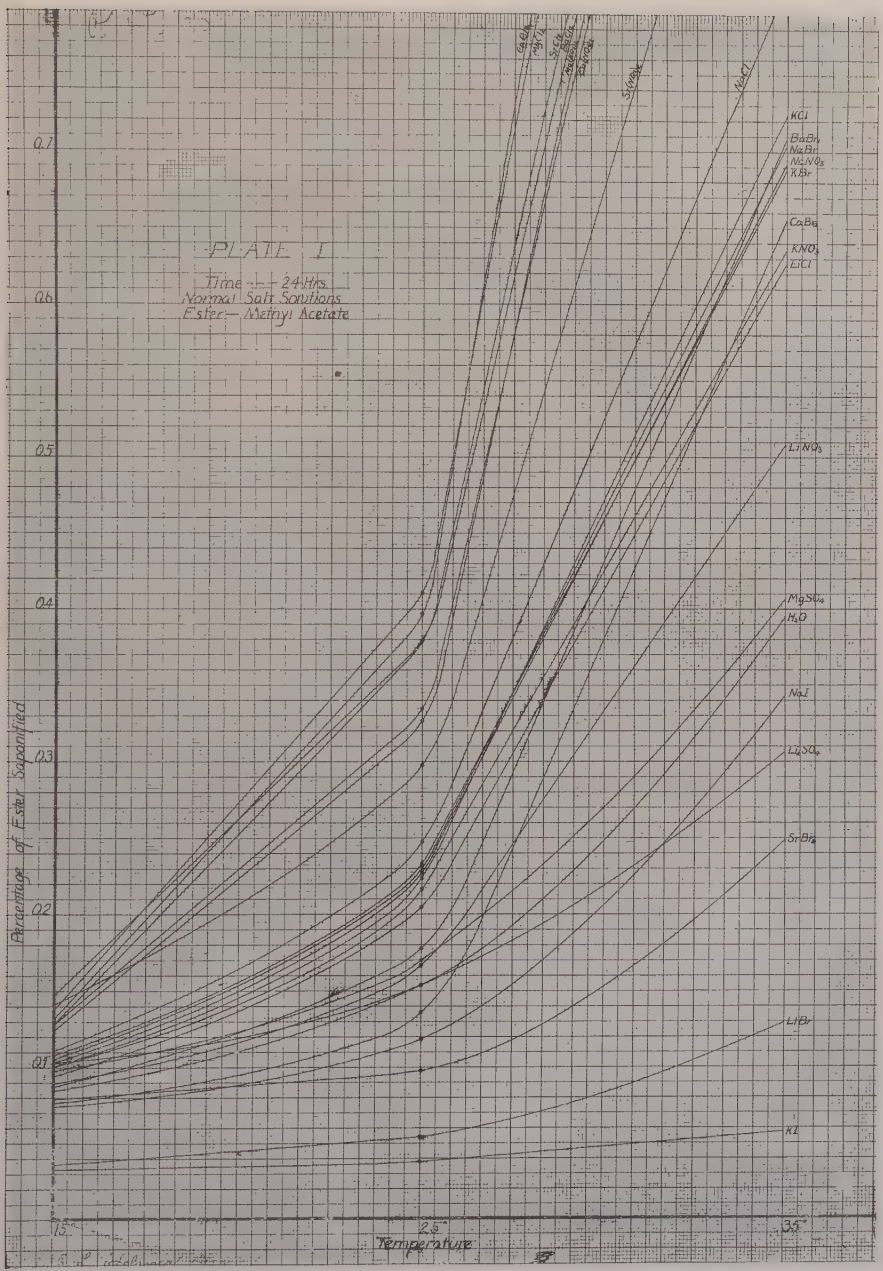
PLATE I
Time - 1 - 24 Hrs.
Normal Salt Solutions
Ester — Methyl Acetate
Percentage of Ester Saponified
Temperature
0.1
0.2
0.3
0.4
0.5
0.6
15°
25°
35°
KCl
BaBr2
NaBr
NaVO3
KBr
CaBr2
KNO3
LiCl
LiNO3
MgSO4
H2O
NaI
Li2SO4
SrBr2
LiBr
KI
NaCl
Strong

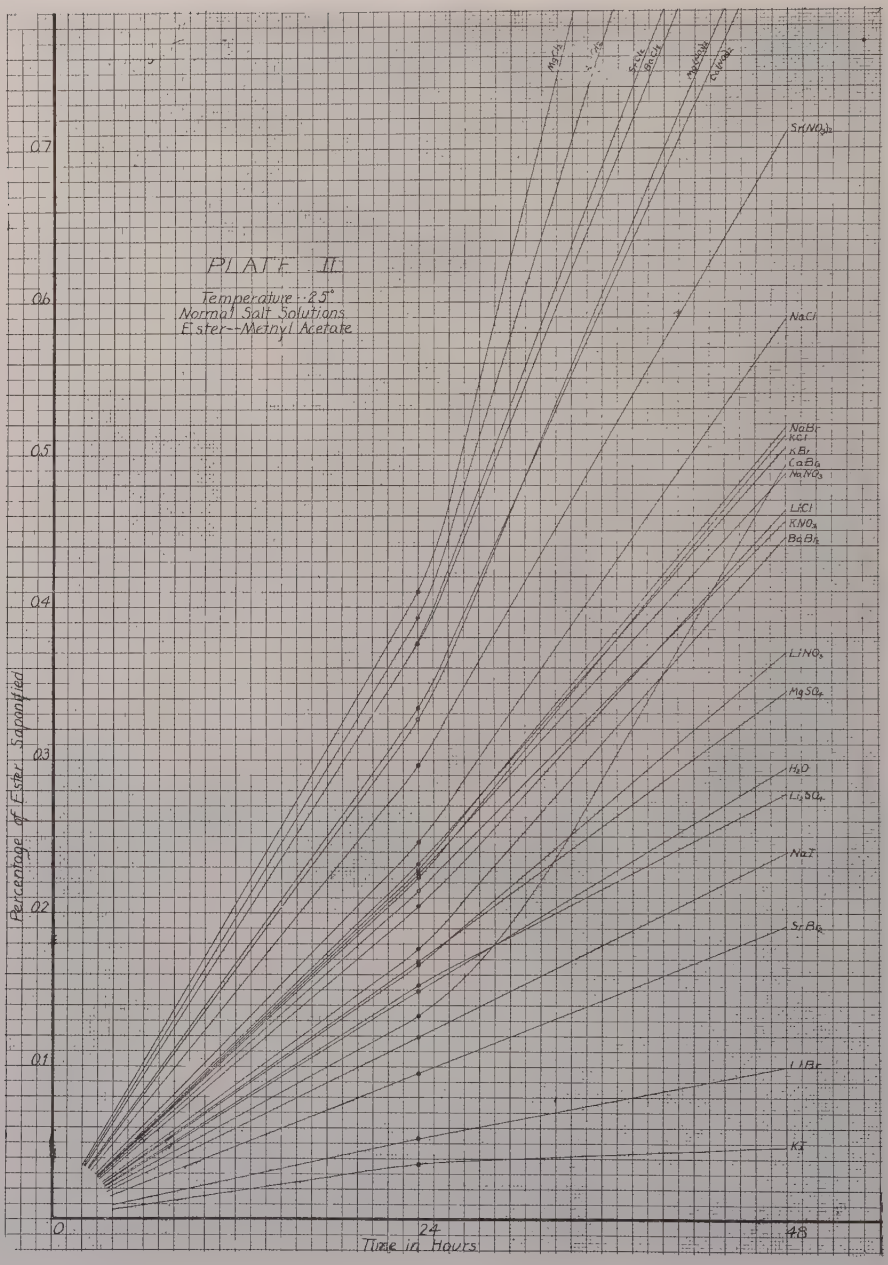
PLATE II
Temperature 25°
Normal Salt Solutions
Ester--Methyl Acetate
Percentage of Ester Saponified
Time in Hours
0
24
48
0.1
0.2
0.3
0.4
0.5
0.6
0.7
MgCl2
CaCl2
SrCl2
BaCl2
CuSO4
Sr(NO3)2
NaCl
NaBr
KCl
KBr
CaBr2
NaNO3
LiCl
KNO3
BaBr2
LiNO3
MgSO4
H2O
Li2SO4
NaI
SrBr2
LiBr
KI

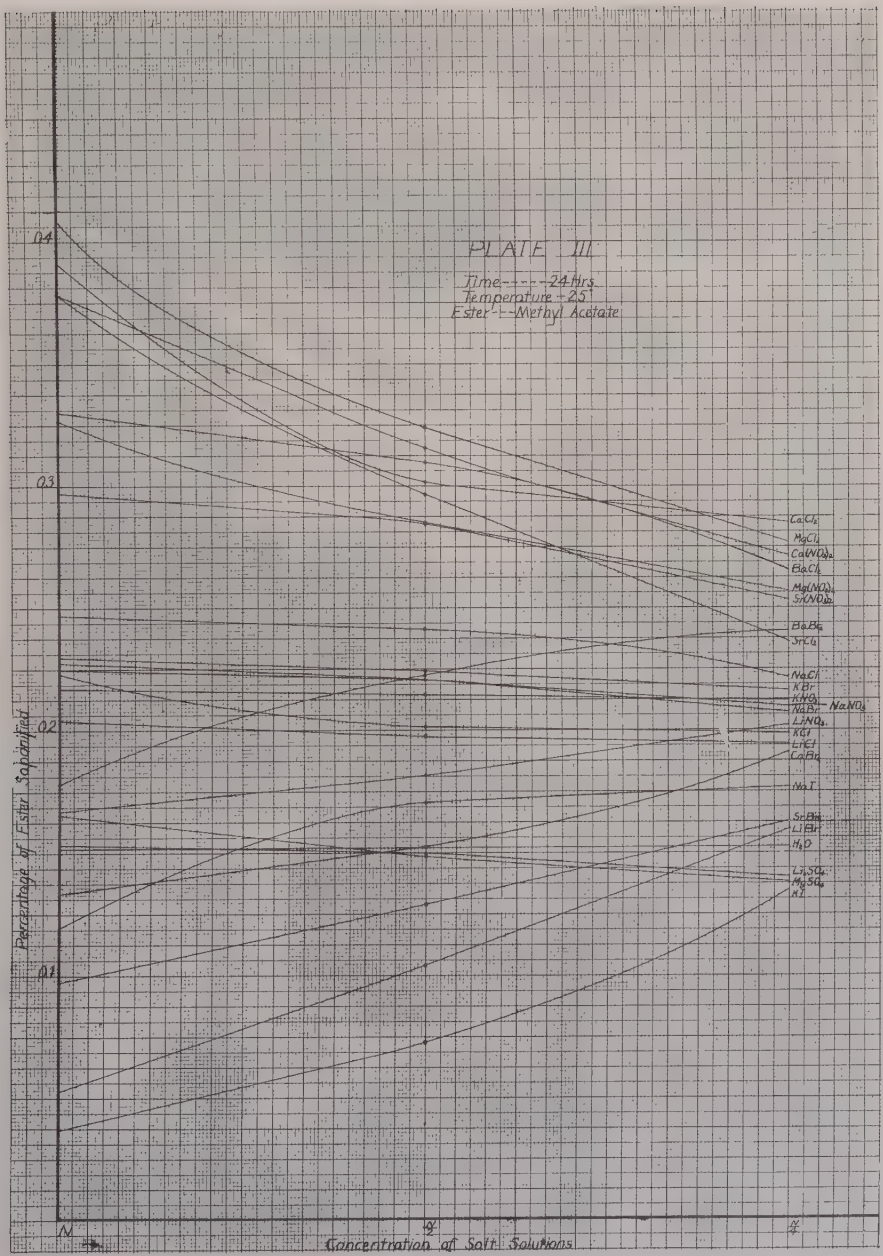
PLATE III
Time-----24 hrs.
Temperature-25°
Ester'---Methyl Acetate
0.4
0.3
0.2
0.1
Percentage of Ester Saponified
N
½
¼
Concentration of Salt Solutions
CaCl2
MgCl2
Ca(NO3)2
BaCl2
Mg(NO3)2
Sr(NO3)2
BaBr2
SrCl2
NaCl
KBr
KNO3
NaBr
NaNO3
LiNO3
KCl
LiCl
CaBr2
NaI
SrBr2
LiBr
H2O
Li2SO4
MgSO4
KI

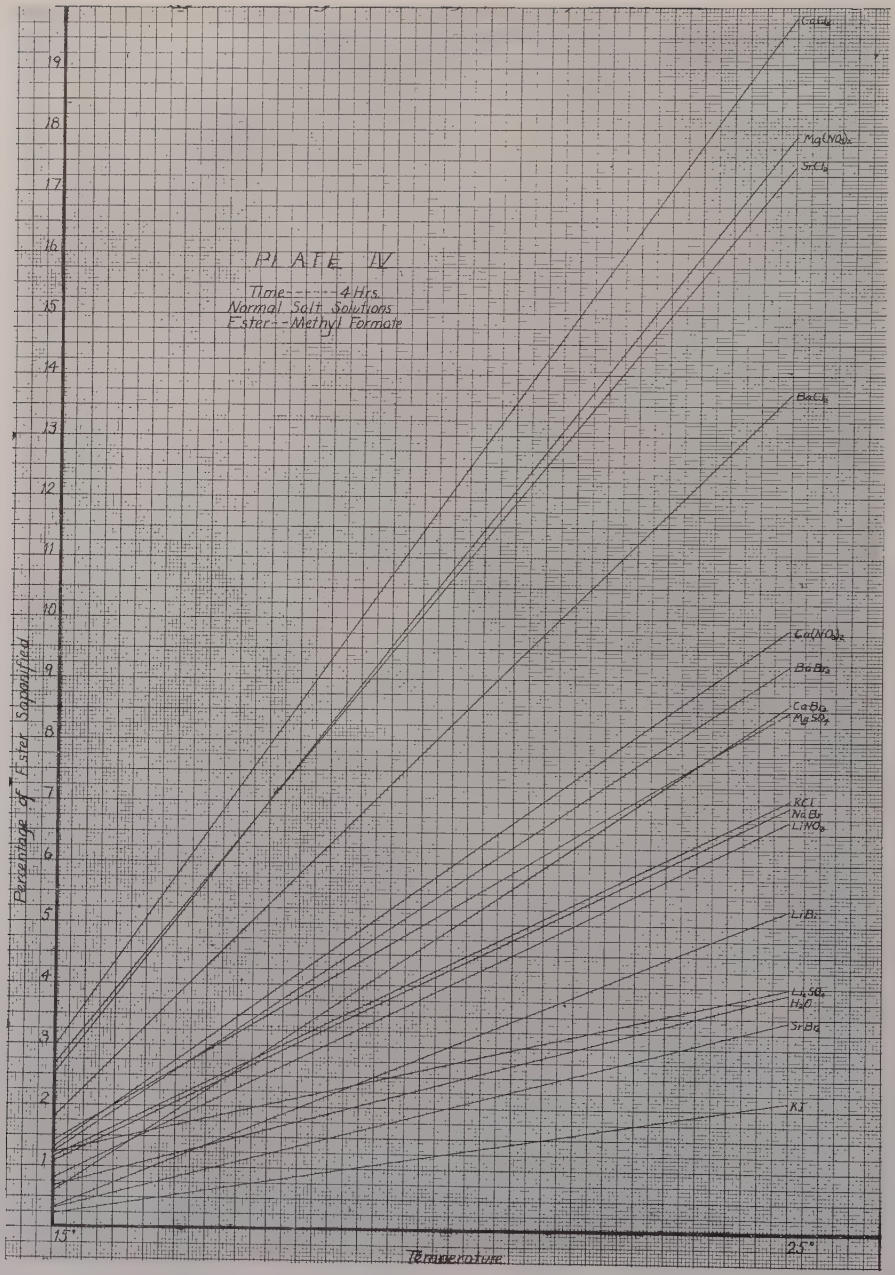
PLATE IV
Time-----4 Hrs.
Normal Salt Solutions
Ester--Methyl Formate
Percentage of Ester Saponified
Temperature
15°
25°
$CaCl_2$
$Mg(NO_3)_2$
$SrCl_2$
$BaCl_2$
$Ca(NO_3)_2$
$BaBr_2$
$CaBr_2$
$MgSO_4$
KCl
NaBr
$LiNO_3$
$LiBr$
Li_2SO_4
H_2O
$SrBr_2$
KI

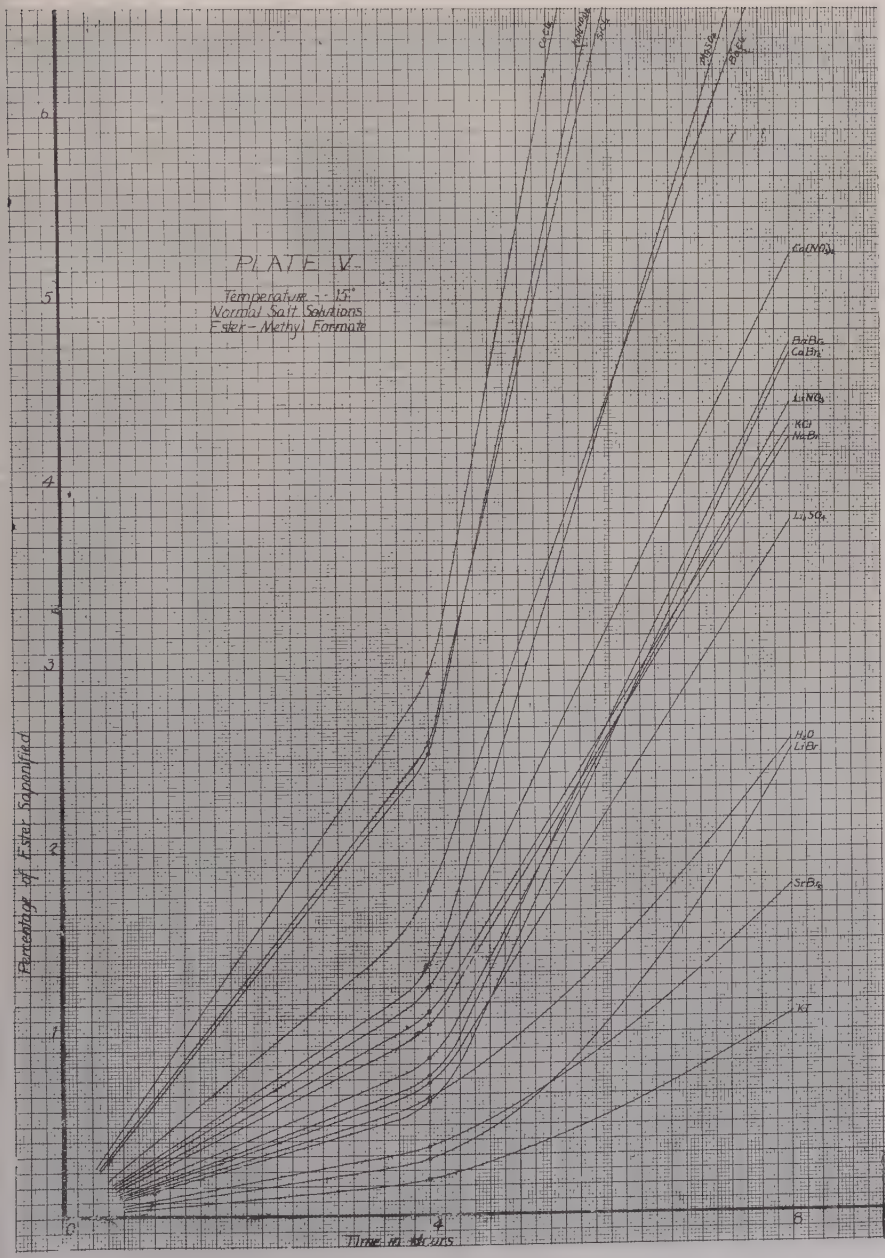
PLATE V.
Temperature -- 15°
Normal Salt Solutions
Ester - Methyl Formate
Percentage of Ester Saponified
Time in Hours
0
1
2
3
4
5
6
$Cu(NO_3)_2$
$BaBr_2$
$CaBr_2$
$LiNO_3$
KCl
NaBr
Li_2SO_4
H_2O
LiBr
$SrBr_2$
KI

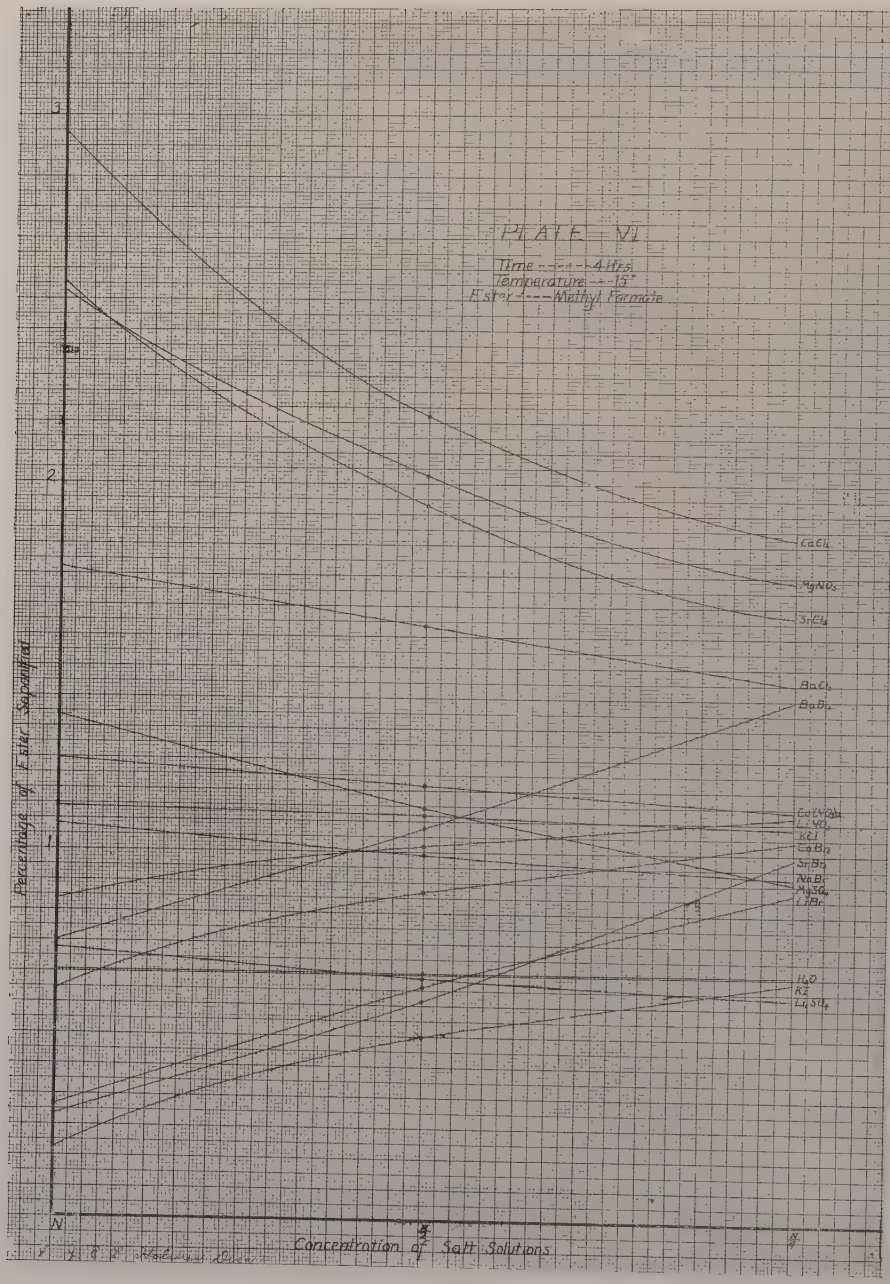
PLATE VI
Time - - - - 4 Hrs.
Temperature - - 15°
Ester - - - - Methyl Formate
Percentage of Ester Separated
Concentration of Salt Solutions
CaCl2
Mg(NO3)2
SrCl2
BaCl2
BaBr2
Ca(NO3)2
LiNO3
KCl
CaBr2
SrBr2
NaBr
MgSO4
LiBr
H2O
KI
Li2SO4

Discussion of Results

From Plates I and II the salts which produce the greatest increase in velocity, and which have the largest temperature coefficients, are magnesium chloride, calcium chloride, strontium chloride, barium chloride, magnesium nitrate, calcium nitrate, and strontium nitrate. All of these salts crystallize with water of crystallization, varying from six to two molecules each. Next come salts that do not have water of crystallization, as sodium chloride, sodium nitrate, potassium chloride, and potassium bromide. Along with these salts we have some that have water of crystallization, as sodium bromide, calcium bromide, lithium chloride, lithium bromide, lithium nitrate, and magnesium sulphate, which seem to be exceptions in the light of the action of the other salts that crystallize with water.

Still more inexplicable seem to be the curves for lithium sulphate, sodium iodide, strontium bromide, lithium bromide, and potassium iodide, since these curves are below the curve for pure water.

Let us now consider Plate III. As the dilution is increased, salts such as magnesium chloride show a marked decrease in velocity; the salts with no water of crystallization show a less decrease, while the apparent exceptions, such as calcium bromide, strontium bromide, etc., show a marked increase in velocity, most of their curves ending above the curve for water.

Let us now consider the salts of any one metal (Plates I and II), *e. g.*, calcium. The chloride increases the velocity more than the nitrate, the nitrate more than the bromide. With potassium and sodium, the chloride has more effect than the nitrate; the nitrate more than the bromide; the bromide more than the iodide. Of the salts studied, the sulphates seem to have the least effect. There also seems to be a general relation between the metals themselves, as magnesium, calcium, strontium, and barium, though in the series lithium, sodium, and potassium, lithium seems to be an exception.

The curves for the methyl formate are of the same general character, the only difference being that the curves are more extended, more being above the curve for water, probably

due to the larger amount of saponification. The curves for calcium bromide, barium bromide, and magnesium sulphate with methyl formate do not seem to be exceptions, as they fall above the curves for salts with no water of crystallization.

Kellogg[1] found in the case of the halides of potassium, that the chloride increased the reaction the most, the bromide less and the iodide least, normal potassium iodide actually decreasing the velocity. This seems to point to the fact that the anion plays an important part in the total effect of the salt on the reaction velocity. With more dilute solutions of potassium iodide (0.25 N) the velocity of the reaction is increased. Kellogg's curves for strontium chloride, calcium chloride, and barium chloride show that the cation must also be taken into account. A possible explanation of the behavior of barium bromide, calcium bromide, etc., may be that the total effect due to these salts is due to a combination between a cation tending to increase the velocity, and an anion tending to decrease the velocity.

Kellogg[1] also finds that there is a concentration for each salt that will produce the greatest increase in the velocity of the reaction. Still further increase or decrease of the concentration from this point diminishes the velocity of the reaction.

The action of the apparent exceptions which manifested themselves in the study of this problem, *i. e.*, lithium nitrate, lithium bromide, calcium bromide, etc., may be due to the concentration of maximum saponification not having been reached, since these salts on dilution all increase the velocity.

Altogether, it is probable that had the dilution been still farther increased, the apparent exceptions would have proved not to be exceptions at all. This seems to be all the more true, in that the curves of Plate IV, where larger percentages of methyl formate are saponified, show that barium bromide, calcium bromide, and magnesium sulphate have greater effect than potassium chloride and sodium bromide.

Therefore, it seems more than probable that with solutions dilute enough to reach the dilution of maximum saponifica-

[1] *Jour. Amer. Chem. Soc.*, **31**, 886 (1909); **35**, 396 (1913).

tion, and with a larger amount of ester saponified, most of the apparent exceptions on Plates I and II would no longer be exceptions; but we would have a general relation between salts with water of crystallization and salts without, the former increasing the velocity to a larger extent than the latter, having a larger temperature coefficient and decreasing more with dilution.

We are not satisfied with the results with strontium bromide and hope in the near future to do more work with this salt.

The position of the curve for a salt seems then to be a function of its water of crystallization, supplemented by an effect due to the ions it forms, *e. g.*, water of crystallization would place the curve above the curves of salts that do not have water of crystallization; the anion $\overset{-}{Cl}$ would place it above a salt with an anion $\overset{-}{NO_3}$ or $\overset{-}{Br}$; and the cation $\overset{++}{Mg}$ would place it above a salt with a cation $\overset{++}{Ca}$, $\overset{++}{Sr}$ or $\overset{++}{Ba}$.

This general relation seems to hold among the salts that have no water of crystallization. On Plate I and II the lithium salts do not seem to fit in with the sodium and potassium salts, but what has been said about calcium bromide and barium bromide applies also to these salts as is shown by Plates III, IV and V.

How can we explain this increase in the velocity of the reaction caused by salts that have water of crystallization, and the decrease in their effect on dilution?

Getman and Bassett[1] showed that the salts having water of crystallization are in solution the most hydrated. Assuming that the effect of the salts with water of crystallization is due to their being hydrated, let us see what we would expect.

(1) According to Getman and Bassett, the chlorides, nitrates, etc., of such salts as magnesium, calcium, strontium, and barium would increase the velocity of the reaction, with results that are very nearly the same, much more than the non-hydrated salts.

(2) As the concentration decreases, the effect would be

[1] *Carnegie Inst. Wash. Pub.* No. 60, 15 (1907).

lessened, since the total combined water would be less, the decrease being much more rapid than in the case of non-hydrated salts.

(3) From the work of Pearce,[1] who showed that the hydrating power of a cation is inversely proportional to its atomic volume, we should expect the curves for the salts of magnesium, calcium, barium, and strontium with a common anion, to give curves similar to those found by him, *i. e.*, magnesium salts have the greatest effect, then calcium, strontium, and barium.

Let us see if the experimental data confirm these conclusions, based on the assumption that the difference in action between salts that have water of crystallization and salts that do not is due largely to the hydrates formed by the salts with water of crystallization.

Taking into consideration the facts brought out earlier, that the dilution of maximum saponification for the apparent exceptions had not been reached, and that larger percentages of ester saponified would also tend to make the apparent exceptions not real, we can draw from the curves the following conclusions:

(1) Salts with water of crystallization increase the velocity of the reaction much more than salts without water of crystallization.

(2) The effect of salts with water of crystallization decreases, on dilution, much more than the salts without water of crystallization.

(3) Among the metals with common anions, as magnesium, calcium, strontium, and barium chlorides or nitrates, the curves are arranged in the order of the decreasing atomic weights of the cations.

We, therefore, conclude that the difference in action between salts with water of crystallization, and salts without, on the saponification of esters is due to the chemical difference between hydrated and non-hydrated salts, or between free and combined water.

As an explanation of this difference in action we offer the suggestion that the combined water is more highly ionized

[1] *Carnegie Inst. Wash. Pub.* No. 180, 57 (1913).

than free water, and with hydrated salts we have this effect added to the salt effect shown in the case of non-hydrated salts.

Pearce[1] shows that the cations are the ones that are hydrated, the anions, if hydrated at all, being only slightly hydrated.

The curves we find for the halides of potassium show that in the saponification of esters, the anions play an important part. This is in line with what Kellogg[2] found.

It, therefore, seems probable that the anions are also hydrated to a certain extent.

But how can the larger temperature coefficient of reaction velocity of the hydrated salts be accounted for, since with rise in temperature the hydrates become less complex? A study of Plates II and V shows that, temperature being constant, the amounts of ester saponified in the presence of the hydrated salts, as the time increases, is much greater than the amounts saponified in the presence of the non-hydrated salts.

This is probably due to the larger amount of acid formed by the saponification of the ester by combined water. With rise in temperature the larger amount of acid would give us a larger temperature coefficient. Another factor to be taken into consideration is the hydrolysis of the hydrated salts which, though negligible at low temperature, increases greatly as the temperature rises. The increased fluidity of the solution must also be taken into account, the hydrates becoming with rise in temperature less complex. These three factors would probably offset the decomposition of the hydrates, giving less combined water, with the result that we would have a larger temperature coefficient of reaction velocity for the hydrated salts than the non-hydrated.

From the standpoint of hydrates breaking down with rise in temperature, let us consider the effect of such rise on chemical reactions in general. The influence of temperature on the velocity of reactions is usually very great.

Berthelot[3] showed that the velocity with which an ester is formed is about 22,000 times as great at 200° as at 7°.

[1] *Carnegie Inst. Wash. Pub.* No. **180**, 57 (1913).
[2] *Jour. Amer. Chem. Soc.*, **31**, 886 (1909); **35**, 396 (1909).
[3] *Essai de Mécanique Chimique*, **2**, 93 (1879).

Spohr[1] finds that cane sugar is inverted 5 times as rapidly at 55° as at 25°. Various attempts have been made to explain the effect of rise in temperature on the velocity of chemical reactions. A decrease in the viscosity of the medium with rise in temperature, allowing the ions to move more rapidly, a decrease in the mass of the ion with rise in temperature, and the increased kinetic energy of the molecules and ions, have been cited as the causes of the great increase, with rise in temperature, in reaction velocity. None of these theories seems sufficient to account for such an increase in the velocity of reactions as was noticed by Berthelot and others.

From solvate theory of solution we see that ions and molecules attract to them molecules of the solvent. We would expect these ions to react more slowly, especially if the solvate were very complex since the solvate would act as a protective covering around the ions and diminish the velocity with which they would react with one another. But suppose the temperature is raised, the solvate would become less and less complex, until finally the ions would not have any appreciable protective covering. In such a case, where the ions are in direct contact, we should expect the velocity of the reaction to be greatly increased.

We, therefore, offer this tentative suggestion as one of the most important causes of the increase in the velocity of chemical reactions with rise in temperature.

In conclusion, we can say that the chemical differences between free and combined water, brought out in the study of this problem, are strictly analogous to the physical differences between free and combined water, as shown by their power to absorb light, which led us to investigate this problem.

Summary

The following conclusions have either been confirmed or brought out in this investigation:

(1) The reaction involving the decomposition of an ester proceeds slowly at ordinary temperatures, and, therefore, can be readily and accurately studied.

[1] *Zeit. phys. Chem.*, **2**, 195 (1888).

(2) The hydrolysis of the chlorides and nitrates, etc., of calcium, magnesium, strontium, and barium employed in the study of this problem is so small that it cannot account for the differences observed.

(3) Salts with water of crystallization increase the velocity of the saponification of an ester to a greater extent than salts with no water of crystallization.

(4) On dilution, the effect with salts having water of crystallization decreases more rapidly than with salts without crystal water.

(5) The curves for the saponification of methyl formate are very similar to those for methyl acetate.

(6) The large effect of salts with water of crystallization is probably due in part to their being hydrated, combined water being more highly ionized than free water.

(7) The amount of the saponification and, therefore, the position of the curve seems to be due to the combined effect of both cation and anion.

(8) It is probable that anions as well as cations are hydrated.

(9) The hydration of cations is inversely proportional to their atomic volumes.

(10) There seems to be a dilution of maximum saponification for each salt.

(11) Hydrated salts show a large temperature coefficient, notwithstanding the decomposition of hydrates with rise in temperature.

(12) Decomposition of hydrates may play an important role in the increased velocity of chemical reactions with rise in temperature.

(13) The chemical differences between free and combined water are analogous to the physical differences.

BIOGRAPHY

James Eugene Levering Holmes, the author of this dissertation, was born in Baltimore, Maryland, January 28, 1891. He received his preliminary training in the private schools of Baltimore, graduating from the Gilman Country School in 1908. He entered the Johns Hopkins University in the fall of 1908, and received the degree of Bachelor of Arts in 1912.

He began his work as a graduate student in chemistry in 1912, with physical chemistry and applied electricity as his subordinate subjects.

He received scholarship for the years 1913–14 and 1914–15, and was assistant instructor in chemistry in the Johns Hopkins Summer School in 1914.